

35 U.S.C. §112, first paragraph states that “the specification shall contain a written description of the invention, and of the manner and process of making and using it ... to enable *any person skilled in the art...* to make and use the same...” (emphasis added).

The term “catalyst turnover number” is well known to one skilled in the art as evidenced by the attached list of 335 patents using the term. Pearson et al. U.S. 6,284,919 is attached and is representative of the many U.S. and foreign patent publications that use and describe the term “catalyst turnover number.” The term “catalyst turnover number” is well known to one skilled in the art as evidenced by the attached Hayashi et al. December 24, 1999 article and Mushima et al. 1994 article. These articles are representative of many Google uncovered references that use and define the term.

The terms “catalyst turnover number” and “turnover number” and the TON abbreviation are defined at the Specification page 14, lines 17 to 20 and are exemplified in 55 runs of Example 5 at specification page 15 and in the succeeding selection and by runs by the last paragraph on page 15 to line 8, page 16 and line 25, page 16 to page 17, line 2 of the specification.

The August 10, 2004 Final Rejection fails to indicate in what manner a term as well documented as known in the art and as extensively described and exemplified in the specification fails to meet the requirements of 35 U.S.C. §112, first paragraph. To this extent, the 35 U.S.C. §112, first paragraph rejection is improper examination and an improper final rejection.¹

¹ The MPEP 2271 states:

.... The grounds of rejection must (in the final rejection) be clearly developed to such an extent that the patent owner may readily judge the advisability of an appeal.....

Further, 37 C.F.R. § 1.104 entitled “Nature of Examination” provides that “[t]he examiner's action will be complete as to all matters....”

II. 35 U.S.C. 112, SECOND PARAGRAPH REJECTION

Claims 1 to 12 and 16 to 21 were rejected under 35 U.S.C. §112, second paragraph.

With respect to the specification definition of “catalyst turnover number,” the Final Rejection states that:

Since the language "catalytic turnover number;; appears to be stated in the alternative form (i.e. "or") it is unclear if Applicants intend such language "catalytic turnover number" to be defined as only "the number of moles of aromatic carbonate produced per mole of Palladium catalyst charged" or some other definition or calculation, wherein no further information is disclosed..

August 10, 2004 Final Rejection, page 4.

Applicant believes that the PTO is arguing that the alternative conjunction “or” makes the definition of catalyst turnover number unclear or that the definition of catalyst turnover number indicated at pages 14-15, lines 19 and 1-3 is restricted to “moles of aromatic carbonate produced per mole of Palladium catalyst charged” However, 35 U.S.C. §112, second paragraph only requires that the claims read in light of the specification apprise one “skilled in the art” of the scope of the invention. *Hybritech v. Monoclonal Antibodies, Inc.*, 802 F.2d 1367, 1387, 231 USPQ 81, 94, 95 (Fed. Cir. 1986), cert. denied 480 US 947 (1987). TON may have generic/species meanings depending on context. (Otherwise generic claims would be prohibited.) 35 U.S.C. §112, second paragraph does not prohibit the use of broad. The claims are definite to one skilled in the art. The rejection of claims 1 to 12 and 16 to 21 under 35 U.S.C. §112, second paragraph should be withdrawn.

III. 35 U.S.C. 103(a) REJECTION

Claims 1 to 12 and 16 to 21 were rejected under 35 U.S.C. §103(a) over Cong et al. and Brown et al. and claims 1 to 12 and 16 to 21 were rejected under 35 U.S.C. §103(a) over Nan et al. and Brown et al.

Applicant's May 24 Amendment pointed out that:

.... the references have no *In re Lee* teaching that would have led one skilled in the art to combine the various Cong et al., Brown et al. and Nan et al. teachings. See *In re Lee*, 277 F.3d 1338, 61 USPQ 2d 1430, (Fed. Cir. 2002). Brown does not relate to discovery of catalysts. One skilled in the art would not have been led to "executing a genetic algorithm based on" a "catalyst turnover number" to combinatorially select a best catalyst system by a teaching that does not mention catalysis (Brown et al.). This is particularly so in the unpredictable field of catalytic chemistry. See *In re Marzocchi*, 439 F.2d 220, 223-24, 169 USPQ 367, 369-70 (CCPA 1971).

May 24 Amendment, page 9.

In response, the Final Rejection first acknowledges at page5 that "...Brown et al. does not specifically direct the described method of designing combinatorial library mixtures...." Then purportedly in response to *In re Lee* requirements, states:

Brown et al. does disclose: 1) the application of the method to the optimization of any number of physical or other properties of the combinatorial library (catalytic property, catalytic turnover number, halide, etc; Abstract; and pages 2305-2308)...and 2) indicates the successful application of genetic algorithms to a wide range of problems in both chemical and non~chemical domains.

This characterization of the Brown et al. teaching is incorrect. Nowhere does Brown et al. mention "catalytic property, catalytic turnover number, halide etc." The reference in the Brown et al. abstract to "any property" has to do with "properties of the library." The library is an array of synthesized products. The meaning of "properties: is not that Brown et al. is applicable to discovering a catalyst; only that the Brown et al. process is applicable to improving any property of the product of the Brown et al. *synthesis*.

Further, Applicant has been unable to identify a teaching of Brown et al. that "indicates the successful application of genetic algorithms to a wide range of problems in both chemical and non~chemical domains." In accord with law and practice, the PTO is requested to identify the language in Brown et al. that purportedly teaches or suggests "the successful application of genetic algorithms to a wide range of problems in both

chemical and non-chemical domains,” or withdraw the rejection. See 37 CFR 1.104 entitled “Nature of examination” and *In re Rijckaert*, 28 USPQ2d 1955, (Fed. Cir. 1993).².

The Final Rejection fails to address the question; why would one skilled in the art be led to combine the various Cong et al., Brown et al. and Nan et al. teachings? See *In re Lee*, 277 F.3d 1338, 61 USPQ 2d 1430, (Fed. Cir. 2002). Brown et al. does not relate to discovery of catalysts. One skilled in the art would not have been led to “executing a genetic algorithm based on” a “catalyst turnover number” to combinatorially select a best catalyst system by a teaching that does not mention catalysis (Brown et al.). this is particularly so in the unpredictable field of catalytic chemistry. See *In re Marzocchi*, 439 F.2d 220, 223-24, 169 USPQ 367, 369-70 (CCPA 1971).

Further, Applicant’s May 24 Amendment pointed out that:

... even if improperly combined, the reference s do not teach or suggest “executing a genetic algorithm based on” a “catalyst turnover number.” The references do not establish a prima facie case of obviousness. See *In re Oetiker*, 977 F.2d 1443, 24 USPQ2d 1443 (Fed. Cir. 1992).

May 24 Amendment, page 9.

The Final Rejection does not respond to this argument. The Final Rejection should be withdrawn and the claims allowed or another office action issued to addresses all Applicant’s arguments,

For these reasons, the rejections of claims 1 to 12 and 16 to 21 under 35 U.S.C. §103(a) over Cong et al. and Brown et al. and claims 1 to 12 and 16 to 21 under 35 U.S.C. §103(a) over Nan et al. and Brown et al. should be withdrawn.

IV. PREMATURE FINAL REJECTION

2 .” “[W]hen the PTO asserts that there is an explicit or implicit teaching or suggestion in the prior art, it must indicate where such a teaching or suggestion appears in the reference....” *In re Rijckaert*, 28 USPQ2d *supra* at page 1957.

The Final Rejection (1) fails to indicate in what manner “catalyst turnover number” fails to meet the requirements of 35 U.S.C. §112, first paragraph and (2). fails to respond to Applicant’s argument that even if improperly combined, the reference s do not teach or suggest “executing a genetic algorithm based on” a “catalyst turnover number.” The references do not establish a prima facie case of obviousness. *See In re Oetiker*, 977 F.2d 1443, 24 USPQ2d 1443 (Fed. Cir. 1992).

MPEP 2271 states:

In making the final rejection, all outstanding grounds of rejection of record should be carefully reviewed and any grounds of rejection relied on should be reiterated. The grounds of rejection must (in the final rejection) be clearly developed to such an extent that the patent owner may readily judge the advisability of an appeal.... [T]he final rejection... *should include a rebuttal of any arguments raised in the patent owner's response.* (Emphasis added.)

37 C.F.R. § 1.113 entitled “Final rejection or action” provides that “ the examiner shall repeat or state all grounds of rejection then considered applicable to the claims in the application, *clearly stating the reasons in support thereof.* (Emphasis added.)

37 C.F.R. § 1.104 entitled “Nature of Examination” provides that “[t]he examiner's action will be complete as to all matters....”

Applicant requests the PTO to withdraw the present Office Action and to either allow the claims or issue a complete office action, restarting the period for response to address (1) the PTO failure to indicate in what manner “catalyst turnover number” fails to meet the requirements of 35 U.S.C. §112, first paragraph and (2).the PTO failure to respond to Applicant’s argument that even if improperly combined, the reference s do not teach or suggest “executing a genetic algorithm based on” a “catalyst turnover number.” The references do not establish a prima facie case of obviousness In this respect, Applicants include with this Amendment, an MPEP 706.07(c) AND MPEP 706.07(d) REQUEST TO WITHDRAW FINAL REJECTION addressed to the Supervisory Primary Examiner. This REQUEST is filed pursuant to MPEP 706.07(c) and MPEP


706.07(d) as prerequisite to a Petition to the Commissioner of Patents.

V. CONCLUSION

In view of the foregoing amendments and remarks, it is respectfully submitted that claims 1 to 12 and 16 to 21 are allowable. Reconsideration and allowance are requested.

Should the Examiner believe that any further action is necessary in order to place this application in condition for allowance, he is requested to contact the undersigned at the telephone number listed below.

Respectfully submitted,



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High turnover number of γ -SiW₁₀{Mn^{III}(OH₂)₂O₃₈}⁶⁻ for oxygenation of cyclohexane with 1 atm molecular oxygen†

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Received (in Cambridge, UK) 24th December 1999, Accepted 3rd February 2000

An all-inorganic oxo-bridged dimanganese-containing silicotungstate, γ -SiW₁₀{Mn^{III}(OH₂)₂O₃₈}⁶⁻, showed the highest turnover number of 789 among various metal-substituted silicotungstates for the oxygenation of cyclohexane with 1 atm molecular oxygen; this is the highest level when compared with other catalysts reported so far.

Catalytic oxygenation of alkanes has attracted much attention. The utilization of molecular oxygen for catalytic oxygenation is a rewarding goal because among oxidants molecular oxygen has the highest content of active oxygen and forms no by-products.^{1–7} Reducing reagents or radical initiators have been added for in an attempt to facilitate reaction lowering the reaction temperature and resulting in the suppression of overoxidation of oxygenated products.^{8–13} However, there are only a few examples of ideal homogeneous oxygenation systems for alkanes with molecular oxygen in the absence of reducing reagents or radical initiators because of catalyst deactivation and difficulty of C–H bond/oxygen activation.^{1–24} The oxidation of cyclohexane has been industrialized by using a cobalt catalyst with pressurized molecular oxygen above 423 K, low conversions, however, are a drawback in suppressing overoxidation of the products.^{5,25,26} It is clearly desirable if oxygenation can be carried out with higher turnover numbers under milder conditions. Fe(DPA) (DPA = 2,6-dicarboxylatopyridine), K[Ru^{III}(saloph)Cl₂] [saloph = *N,N'*-*o*-phenylenebis(salicylideneaminato)] PW₉O₃₇{Fe_{3–5}Ni₂(OAc)₃}^{(9+x)-} (*x* = predominantly 1) and γ -SiW₁₀{Fe^{III}(OH₂)₂O₃₈}⁶⁻ are examples of catalysts for cyclohexane oxygenation with 1 atm molecular oxygen.^{14–16,20†} Cobalt-containing aluminophosphate and [Co(NCMe)₄](PF₆)₂ have also been reported to be active for oxygenation of cyclohexane with pressurized molecular oxygen.^{21–24} However, the turnover numbers are low at <180.

Little is known of the structures of the active manganese centers for the oxygenation of cyclohexane with molecular oxygen. Here, we report that the oxo-bridged dimanganese-containing silicotungstate, γ -SiW₁₀{Mn^{III}(OH₂)₂O₃₈}⁶⁻, can efficiently catalyze the oxygenation of cyclohexane with 1 atm molecular oxygen.

Cyclohexane was distilled and treated with activated alumina to remove impurities and cyclohexyl hydroperoxide. The other reagents were commercially obtained and used as received. The reaction was carried out in a glass vial containing a magnetic stir bar as described previously.²⁷ The reaction solution was periodically sampled and analyzed by gas chromatography on TC-WAX capillary columns. The oxidation of cyclohexane did not proceed without catalyst under the present conditions.

Cyclohexanol and cyclohexanone were mainly formed after an induction period for the catalytic oxygenation of cyclohex-

ane with 1 atm molecular oxygen catalyzed by γ -SiW₁₀{Mn^{III}(OH₂)₂O₃₈}⁶⁻ at 365 K. Only small amounts of dicyclohexyl and cyclohexyl hydroperoxide were observed and neither acids, oxoesters nor carbon oxides were observed. The selectivities changed little with time. The conversion was 6.4%, and the turnover number of γ -SiW₁₀{Mn^{III}(OH₂)₂O₃₈}⁶⁻ reached 789 after 96 h, much higher than values reported for the oxygenation of cyclohexane catalyzed by Fe(DPA)/O₂ (1 atm),¹⁴ K[Ru(saloph)Cl₂]/O₂ (1 atm),¹⁵ γ -SiW₁₀{Fe^{III}(OH₂)₂O₃₈}⁶⁻/O₂ (1 atm),²⁰ [Co(NCMe)₄](PF₆)₂/O₂ (3 atm)²¹ or cobalt-containing aluminophosphate/O₂ (15 atm).²³ In addition, the value was higher than those of 130, 90, 5 and 3 reported for Mn(acac)₂/NHPI (NHPI = *N*-hydroxyphthalimide),¹¹ Co(acac)₂/NHPI,¹³ [Fe(HBPz₃)(hfacac)₂O]/Zn (HBPz₃ = hydrotris(1-pyrazolyl)borate, hfacac = 1,1,1,5,5,5-hexafluoroacetylacetone)²⁸ and [R_fMn(R_fTACN)]^{2†}/TBHP (R_fTACN = tris-*N*-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptafluoroundecyl)-1,4,7-triazacylononane; R_f = C₈F₁₇)¹² systems, respectively, which work in the presence of reducing reagents or radical initiators with 1 atm molecular oxygen.

The oxygenation of cyclohexane with 1 atm molecular oxygen proceeded catalytically even at 305 K, whilst no oxygenation was observed for γ -SiW₁₀{Fe^{III}(OH₂)₂O₃₈}⁶⁻ at the same temperature. It has been reported that the commercial catalyst, Co(oct)₂ (oct = 2-ethylhexyl octanoate), was inactive at 348 K with 3 atm molecular oxygen.²¹ All these results demonstrate that γ -SiW₁₀{Mn^{III}(OH₂)₂O₃₈}⁶⁻ can catalyze the selective oxygenation of cyclohexane with high turnover number and under mild conditions.

Table 1 compares turnover numbers for cyclohexane oxygenation with molecular oxygen catalyzed by manganese-substituted silicotungstates. The turnover numbers for manganese-substituted silicotungstates decreased in the order γ -SiW₁₀{Mn^{III}(OH₂)₂O₃₈}⁶⁻ > α -SiW₁₁{Mn^{III}(OH₂)₂O₃₉}⁵⁻ > α -SiW₉{Mn^{III}(OH₂)₂O₃₇}⁷⁻ \approx α -SiW₁₂O₄₀⁴⁻ \approx 0. No oxygenation proceeded for γ -SiW₁₀{Mn^{II}(OH₂)₂O₃₈}⁸⁻ in which the oxidation state of manganese is +2. In addition, among *mono*-transition metal-substituted silicotungstates, α -SiW₁₁{Mⁿ⁺(OH₂)₂O₃₉}^{(8–3n)-} (M = Mn³⁺, Fe³⁺, Cu²⁺), the order of turnover numbers was Mn³⁺ > Fe³⁺ > Cu²⁺. These facts show that manganese is an effective element for catalysis and that a dimanganese site with the oxidation state of +3 is the most effective for the oxygenation of cyclohexane with molecular oxygen.

Small amounts of dicyclohexyl, which is formed by the reaction of two cyclohexyl radicals, and cyclohexyl hydroperoxide were observed. The addition of an alkyl-radical scavenger, *p*-tert-butylcatechol, led to complete inhibition. These facts suggest that the reaction includes a radical-chain mechanism. Further mechanistic work is in progress.

We acknowledge Dr C. Nozaki for the preliminary experiments of this work. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

† Electronic supplementary information (ESI) available: preparation and characterization of polyoxometalates. See <http://www.rsc.org/suppdata/cc/a9/a910334i>

Table 1 Oxidation of cyclohexane with molecular oxygen catalyzed by metal-substituted silicotungstates at 356 K^a

Catalyst	Turnover number ^b	Conversion ^c (%)	Selectivity (%)			
			Cyclohexanol	Cyclohexanone	Cyclohexyl hydroperoxide	Dicyclohexyl
[α]-SiW ₁₂ O ₄₀] ⁴⁻	0	0.0	—	—	—	—
[α -SiW ₁₁ {Mn ^{III} (OH ₂)O ₃ }] ⁵⁻	295	2.4	57	41	2	Trace
[γ -SiW ₁₀ {Mn ^{III} (OH ₂) ₂ O ₃ }] ⁶⁻	789	6.4	51	48	1	Trace
[γ -SiW ₁₀ {Mn ^{II} (OH ₂) ₂ O ₃ }] ⁸⁻	0	0.0	—	—	—	—
[α -SiW ₉ {Mn ^{III} (OH ₂) ₃ O ₃ }] ⁷⁻	0	0.0	—	—	—	—
[γ -SiW ₁₀ {Fe ^{III} (OH ₂) ₂ O ₃ }] ^{6-d}	135	1.1	53	47	—	Trace
[γ -SiW ₁₀ {Cu ^{II} (OH ₂) ₂ O ₃ }] ⁸⁻	0	0.0	—	—	—	—

^a Reaction conditions: catalyst, 1.5 μ mol; solvent, 1,2-C₂H₄Cl₂ (1.5 mL–acetonitrile (0.1 mL)); cyclohexane, 18.5 mmol; P(O₂), 1 atm; reaction time, 96 h.

^b Mol of products/mol of catalysts used. ^c Mol of products/mol of cyclohexane used. ^d Cited from ref. 20.


Notes and references

† The turnover numbers for Fe(DPA), K[Ru^{III}(saloph)Cl₂], PW₉O₃₇{Fe_{3-x}-Ni_x(OAc)₃}^{(9+x)-} and γ -SiW₁₀{Fe^{III}(OH₂)₂O₃}⁶⁻, cobalt-containing aluminophosphate and [Co(NCMe)₄](PF₆)₂ catalysts were 0.2 (reaction temperature, 295 K), 18 (298–318 K), 5 (356 K), 135 (356 K), 167 (403 K) and 180 (348 K), respectively.

§ The selectivity to cyclohexanone and turnover number for γ -SiW₁₀{Mn^{III}(OH₂)₂O₃}⁶⁻ catalyst were 100% and 3, respectively, after 96 h.

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Communication a910334I



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Characterization of Silica-supported Rhodium Catalysts Prepared by Alkoxide Method and Particle Size Effect on Vapor Phase Hydroformylation of Ethylene

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[Nippon Kagaku Kaishi, Vol.31, 1994]

Alkoxide techniques were employed to control the particle size of rhodium dispersed on silica. It was confirmed from the TEM observations that the particles in the reduced catalyst were in a uniform size level and the mean particle size could be adjusted in the range of 25-80 Å by changing the rhodium loading from 0.5 to 20.0 wt%. The EXAFS results showed that the rhodium ions were homogeneously dispersed in the gels obtained by a hydrolysis of the mixed solution of rhodium (III) nitrate dissolved in trimethylene glycol and tetraethyl orthosilicate, leading to a high uniformity of the particle size of rhodium. It was also found that the small metal particles were formed by drying and calcinating the gels and grew by reduction with hydrogen. The turnover number of the gas phase hydroformylation of ethylene grew by reduction with hydrogen. The turnover number of the gas phase hydroformylation of ethylene over the catalyst remarkably increased with a decrease in the metal particle size. (Fig.1) Deposition of carbons onto the surface of the catalyst was observed during the reaction, resulting in a significant reduction of the number of the active site for the reaction.

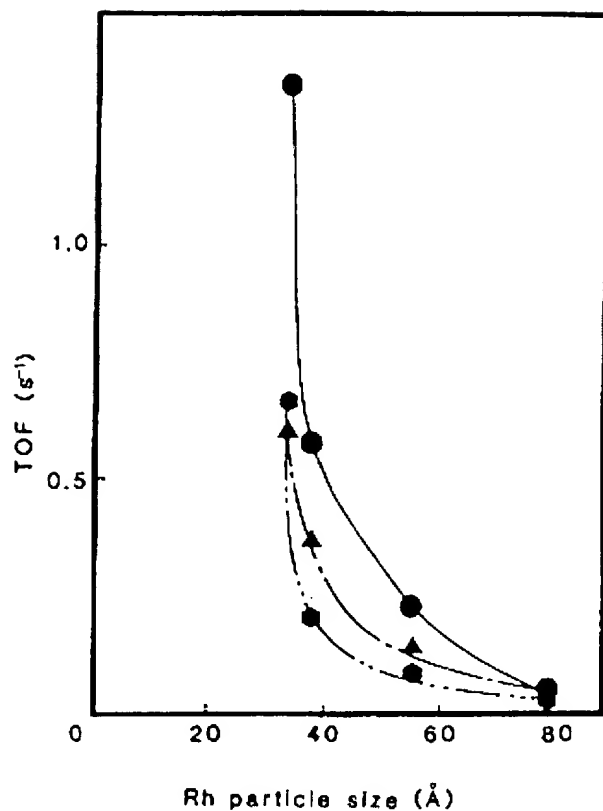


Fig. 1. Dependences of the turnover numbers of vapor phase hydroformylation of ethylene on Rh particle size.

▲, Oxo-Products; ■, Ethane; ●, Ethylene conversion

ABSTRACTS Index